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Rotational dynamics of a discotic liquid crystal studied by deuteron spin relaxation

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We report on measurements of deuteron quadrupolar splitting and spin-lattice relaxation times T_{1Q} and T_{1Z} in the columnar phase of a ring-deuteriated hexaoctyloxyrufigallol at 46 MHz as a function of temperature. To describe small-step rotations of these molecules within each column in the columnar phase, a space-fixed frame is used to diagonalize the molecular diffusion tensor. The principal diffusion constants in this so called 'anisotropic viscosity' model D_α and D_β are for rotations of a molecule around and perpendicular to the columnar axis, respectively. A global target analysis of the spectral densities at seven temperatures in a minimization procedure was carried out. We found that $D_\alpha > D_\beta$, which is consistent with the picture that the motion towards or away from the local director tends to disrupt the packing of molecules within the column.

1. Introduction

The question of how the molecular structure affects the packing and mobility of flat organic molecules in the columnar phase of discotic liquid crystals has recently attracted much attention [1–7]. Studies of molecular ordering and dynamics in liquid crystals have been successfully carried out [8] using multipulse techniques of nuclear magnetic resonance (NMR) spectroscopy. Specifically, deuterium NMR (DMR) and selective chemical deuteriation allow us to investigate a particular site(s) in a molecule and certain aspects of the molecular motion. Hexakis(*n*-hexyloxy)triphenylene (HAT6) has served as a model compound for NMR studies of discotic liquid crystals [5–7]. Recently we have performed a DMR study [4] on a fluorinated version of HAT6, a ring deuteriated 1-fluoro-2,3,7,10,11-hexahexyloxytriphenylene (F-HAT6) and found that the placement of a lateral electric dipole in the triphenylene core drastically modified diffusive rotational motions of these molecules in the columnar phase. It is, therefore, of interest to examine a discotic liquid crystal molecule whose core is substantially different. We have chosen to investigate the core dynamics of a ring-deuteriated hexaoctyloxyrufigallol (see figure 1).

2. Results and discussion

The sample was one used in a previous study [3]. The ring-deuteriated rufigallol has two equivalent deuterons and shows a columnar D_{ho} phase between 305 and 370 K. In the present study, the sample is aligned by cooling from the isotropic phase. The deuterium quadrupolar splitting, the Zeeman (T_{1Z}) and quadrupolar (T_{1Q}) spin-lattice relaxation times are measured at a Larmor frequency of 46 MHz as a function of temperature in the D_{ho} phase of rufigallol. The experimental details can be found elsewhere [9]. Because of the poor signal-to-noise ratio in this sample, an attempt to make T_1 measurements at 15 MHz was not successful. We have carried out a global target analysis [10] of the spectral densities $J_m(m\omega, 90°)$ derived from the T_1 measurements using a rotational diffusion model proposed by Freed *et al.* [11]. This model uses a rotational diffusion tensor for the molecule which is diagonalized in a laboratory frame, typically defined by the local director in the mesophase. Since such a tensor reflects local anisotropies of mesophases, the model is termed the 'anisotropic viscosity' model. It was found [4] that the model can describe very well the observed spectral densities in HAT6 and F-HAT6, and the results for rufigallol using the same model are reported here.

The quadrupolar splitting of the aromatic deuterons in rufigallol is plotted against temperature in figure 1. Since a chain-deuteriated rufigallol sample is unavailable, we cannot determine the order parameter tensor for the entire molecule. The molecular core of rufigallol has C_{2h} symmetry. By choosing the molecular z axis perpendicular to the aromatic ring plane, and the x and y axes to lie on this plane as shown in figure 1, the local order parameter tensor has three non-zero parameters S_{zz}, $S_{xx} - S_{yy}$ and S_{xy}. However as the C–D bond lies along

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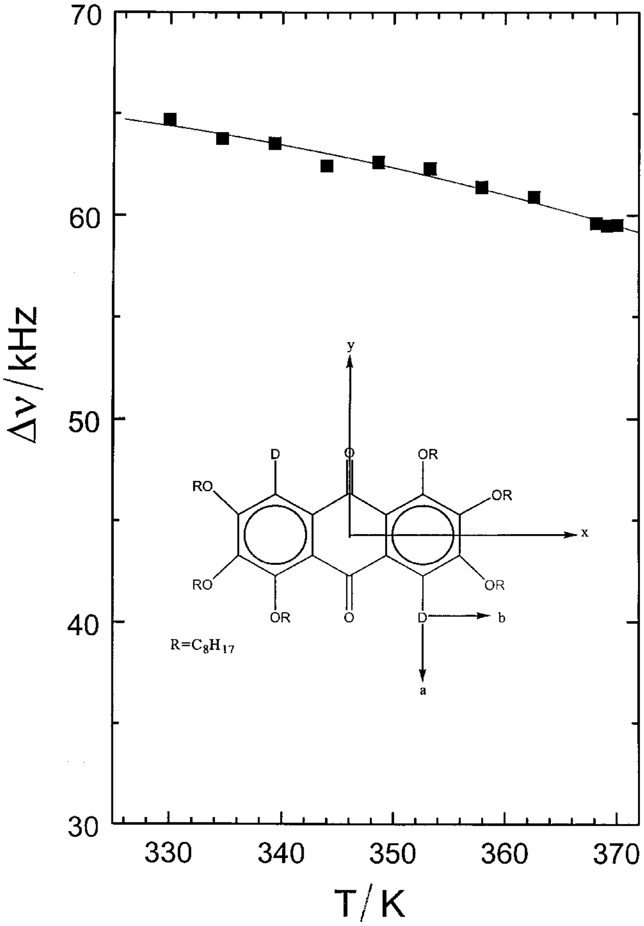

Figure 1. Plot of the quadrupolar splitting versus temperature in the columnar phase of ring deuteriated rufigallol and its molecular structure. The solid line is drawn to aid the eye.

the y axis, we find [12] that the ring deuteron splitting is unaffected by S_{xy} and is given by

$$\Delta\nu = -\frac{3}{8} q_{\mathrm{CD}} [(1+\eta) S_{zz} + (1-\eta/3)(S_{xx} - S_{yy})] \quad (1)$$

where $q_{\mathrm{CD}} = q_{aa}$ and $\eta = (q_{bb} - q_{cc})/q_{aa}$ in the (a, b, c) frame of the quadrupolar interaction tensor. The above expression takes into account that the anisotropy of the molecular diamagnetic susceptibility ($\Delta\chi$) of rufigallol is negative, i.e. the mesophase directors **n** are aligned orthogonally with the applied magnetic field forming a planar distribution. Since it is impossible to obtain both S_{zz} and $S_{xx} - S_{yy}$ from a single splitting, we make the assumption that $S_{xx} - S_{yy}$ is small so that

$$|\Delta\nu| = \frac{3}{8} q_{\mathrm{CD}} (1+\eta) \langle P_2 \rangle \quad (2)$$

where $\langle P_2 \rangle = S_{zz}$ is used. Such an assumption appears [3, 4] to give a good estimate of the molecular ordering in $\mathrm{D_{ho}}$ phases, in particular in view of the insensitivity of rotational dynamics on the molecular biaxiality $S_{xx} - S_{yy}$. Using a quadrupolar coupling constant $q_{\mathrm{CD}} =$ 185 kHz and an asymmetry parameter $\eta = 0.064$ for the ring deuterons, the $\langle P_2 \rangle$ value ranges between 0.81 and 368 K and 0.87 at 332 K. The relations between the relaxation rates and the spectral densities as given by the general relaxation theory are

$$\begin{aligned} T_{1\mathrm{Q}}^{-1} &= 3J_1(\omega_o, 90°) \\ T_{1\mathrm{Z}}^{-1} &= J_1(\omega_o, 90°) + 4J_2(2\omega_o, 90°) \end{aligned} \quad (3)$$

where $\omega_o/2\pi$ is the Larmor frequency. The above measured spectral densities can be written in terms of $J_m(\omega, 0°) \equiv J_m(\omega)(m = 0, 1, 2)$ when the director is aligned along the external magnetic field, as follows [13]

$$\begin{aligned} J_1(\omega, 90°) &= \frac{1}{2}[J_1(\omega) + J_2(\omega)] \\ J_2(2\omega, 90°) &= \frac{3}{8} J_0(2\omega) + \frac{1}{2} J_1(2\omega) + \frac{1}{8} J_2(2\omega). \end{aligned} \quad (4)$$

The derived spectral densities $J_1(\omega_o, 90°)$ and $J_2(2\omega_o, 90°)$ from the deuteron spin-lattice relaxation rates in equation (2) are plotted as a function of temperature in figure 2. It is clear that $J_1(\omega_o, 90°)$ is much larger (by a factor of five to ten) than $J_2(2\omega_o, 90°)$ over the studied temperature range. According to the 'anisotropic viscosity' model, the spectral densities for the aromatic deuteron(s) $J_n(\omega)(n = 0, 1, 2)$ can be written [4] using the notation given in [14] as

$$J_n(\omega) = \frac{3\pi^2}{2} q_{\mathrm{CD}}^2 \sum_m [d^2_{m0}(\beta_{\mathrm{M,Q}})]^2 \sum_K \frac{(B^2_{mn})_K (A^2_{mn})_K}{(A^2_{mn})^2_K + \omega^2} \quad (5)$$

where $\beta_{\mathrm{M,Q}} = 90°$ is the angle between the C–D bond and the molecular z axis, the projection indices m and n refer to the molecular and laboratory frames, respectively, $(A^2_{mn})_K/D_\beta$, the decay constants, are the eigen values and $(B^2_{mn})_K$, the relative weights of the exponentials, are the corresponding eigen vectors from diagonalizing a properly symmetrized Γ_Ω matrix whose elements are formed using a Wigner basis set. The solutions of the rotational diffusion equation are obtained using the computer program given in [14] with the appropriate modification. The rotational diffusion constants D_α and D_β are the principal elements of the rotational diffusion tensor for symmetric top molecules reorienting in a uniaxial medium. D_α is for diffusive precessional motions of the molecular z axis about the space-fixed z (director) axis, and D_β is for motions of the molecular z axis away or towards the director. The uniaxial potential $U(\Omega)/kT = a_{20}(3\cos^2\beta - 1)/2$ in the rotational diffusion equation is obtained from a knowledge of $\langle P_2 \rangle$ at each temperature [14].

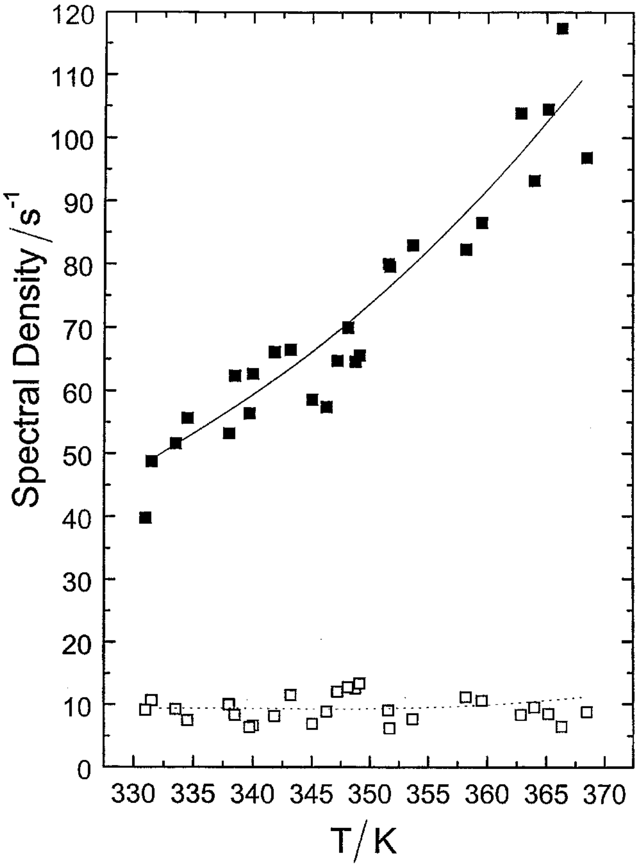

Figure 2. Plots of spectral densities of rufigallol versus temperature at 46 MHz. Closed and open symbols are $J_1(\omega, 90°)$ and $J_2(2\omega, 90°)$, respectively. Solid and dashed curves represent calculated spectral densities based on the anisotropic viscosity model. Experimental uncertainties are reflected in the scatterings of the data points.

In a global target analysis, we take advantage of the fact that the target parameters (D_α, D_β) vary smoothly with temperature to simultaneously analyse data at seven different temperatures covering the columnar phase being studied. This approach was applied previously to HAT6 and F-HAT6 with success, and the rotational diffusion constants obey simple Arrhenius-type relations, giving

$$D_\alpha = D_\alpha^0 \exp(-E_a^\alpha/RT) \tag{6}$$

$$D_\beta = D_\beta^0 \exp(-E_a^\beta/RT). \tag{7}$$

In the above equations, the global parameters are pre-exponentials D_α^0, D_β^0, and their corresponding activation energies E_a^α, E_a^β. As seen before [15], the correlation coefficient between the pre-exponential and its corresponding activation energy is as high as 0.99. Thus, it is advantageous to rewrite equations (6, 7) in terms of the activation energies and the diffusion constants D'_α and D'_β at the highest chosen temperature $T_{\max} = 368$ K. The spectral density data at this particular temperature were first analysed by an individual target analysis to give D'_α and D'_β. A minimization routine [16] (AMOEBA) was used to minimize the sum squared error F

$$F = \sum_k \sum_m [J_m^{\text{calc}}(m\omega_o, 90°) - J_m^{\text{expt}}(m\omega_o, 90°)]_k^2 \tag{8}$$

where the sum over k is for seven temperatures, $m = 1$ or 2. The fitting quality factor Q is given by the percentage mean-squared deviation,

$$Q = 100F \Big/ \sum_k \sum_m [J_m^{\text{expt}}(m\omega_o, 90°)]_k^2. \tag{9}$$

A total of 14 spectral densities is used to derive four global parameters D'_α, D'_β, E_a^α and E_a^β in the minimization giving a $Q = 0.02\%$. The calculated spectral densities from the minimization are shown as solid and dashed curves in figure 2. The fits between calculated and experimental spectral densities are very good because of the small Q. The rotational diffusion constants are plotted versus the reciprocal temperature in figure 3. Again as in HAT6 and F-HAT6, D_α is always larger than D_β, which is consistent with the fact that a change in the β angle would be more disruptive to molecular packings within the column than the precessional motion of the molecular z axis about the columnar axis.

As shown in figure 3, the activation energy for the β-motion E_a^β ($19.4 \pm 1.5\,\text{kJ mol}^{-1}$) is found to be less than that for the α-motion E_a^α ($39.8 \pm 4.9\,\text{kJ mol}^{-1}$). The error limits for a particular global parameter were estimated by varying the one under consideration while keeping all other global parameters identical to those used for the minimum F, to give an approximate doubling in the F value. Now the pre-exponentials in equations (6, 7) are $D_\alpha^0 = 1.77 \times 10^{14}\,\text{s}^{-1}$ and $D_\beta^0 = 9.20 \times 10^9\,\text{s}^{-1}$. The error limits of D_α^0 are 1.68×10^{14} and $1.89 \times 10^{14}\,\text{s}^{-1}$, while those of D_β^0 are 8.94×10^9 and $9.46 \times 10^9\,\text{s}^{-1}$. It is noted that while correlation coefficients between activation energies and their corresponding pre-exponentials are high at near 1, correlation coefficients for the remaining pairs of parameters, i.e. (D_β^0, D_α^0), (D_β^0, E_a^α), (D_α^0, E_a^β), (E_a^β, E_a^α) are about 0.86.

Finally, it may be interesting to compare the core dynamics between HAT6 and rufigallol. Hence, the rotational diffusion constants of HAT6 are reproduced in figure 3 for direct comparison. We note that D_β for rufigallol is a factor of three smaller than that for HAT6, while D_α is about double that for HAT6. The activation energies for these two discotic molecules are very similar. Since D_β is inversely proportional to the rotational viscosity [17], a macroscopic property of liquid crystals, one can infer from our studies that rufigallol is more viscous than HAT6, probably due to entanglements of

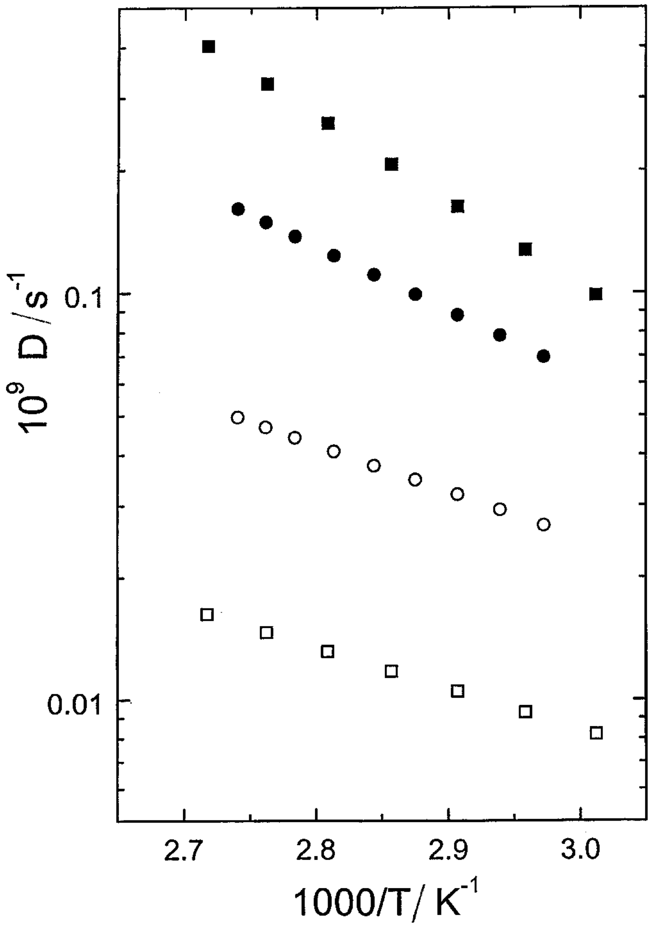

Figure 3. Plots of rotational diffusion constants (squares) versus the reciprocal temperature for rufigallol. The diffusion constants for HAT6 (circles) are reproduced here for comparison. Closed and open symbols denote D_α and D_β, respectively.

side chains within each molecule and with their neighbouring chains on other molecules, as seen in a previous study [3]. The present study, however, has not taken into account effects due to possible density modulations in the column. It would appear that the present relaxation data are insensitive to such slow and collective motions.

3. Conclusion

In conclusion, we have a physical interpretation of the relaxation behaviours of the aromatic deuterons of rufigallol, and the derived model parameters of the anisotropic viscosity model are physically reasonable.

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